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Final Report: Plasmonic Nanocrystals for Enhanced Hybrid Photon Upconversion

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Approved for public release; distribution is unlimited.

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

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a. REPORT	b. ABSTRACT	c. THIS PAGE			MingLee Tang
UU	UU	UU	UU		19b. TELEPHONE NUMBER: 951-827-5964

RPPR Final Report
as of 01-Mar-2018

Agency Code:

Proposal Number: 68838MSREP **Agreement Number: W911NF-16-1-0523**
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DUNS Number: 627797426 EIN: 956006142
Report Date: 30-Nov-2017 Date Received: 12-Dec-2017
Final Report for Period Beginning 01-Sep-2016 and Ending 31-Aug-2017
Title: Plasmonic Nanocrystals for Enhanced Hybrid Photon Upconversion
Begin Performance Period: 01-Sep-2016 **End Performance Period:** 31-Aug-2017
Report Term: 0-Other
Submitted By: MingLee Tang Email: mltang@ucr.edu
Phone: (951) 827-5964
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2 **STEM Participants:** 5

Major Goals: The ultimate goal is to develop an efficient photon upconversion platform that can drastically improve solar cells, photodetectors, photocatalysis, and bioimaging, chiefly by facilitating the use of NIR photons. This will be the first study on plasmon enhanced molecular TTA-based photon upconversion. There is no previous work on this topic because since most experiments are conducted in solution, diffusion makes it difficult to quantify any enhancement when Brownian motion is constantly changing the distance of the light absorber or emitter from the plasmonic structure. This proposal avoids the problems associated with diffusion by considering only photon upconversion in thin films. Here, the focus is on the synthesis and characterization of optical frequency nanoantenna geometries, and their effects on photon upconversion in the solid state. Specific aims are as outlined below:

1) Thin-films with high photon upconversion quantum yield (QY) via the synthesis of:
a. High photoluminescence quantum yield core-shell CdSe-CdS or PbX-CdX nanocrystals &
b. Transmitter ligand architectures that promote triplet energy transfer
A thin film capable of efficiently upconverting NIR and/or visible light to violet light will be synthesized. What is the optimal supramolecular architecture for transferring the triplet exciton from the NC to a molecular transmitter? Are transmitters arranged in linear, two-pronged, multi-armed or branched structures going to show better energy transfer? Can TET be engineered to proceed in one direction only (e.g. from NC to molecule), by employing an energy cascade, or molecular order? Since NCs with high PL QY show the best TET, core-shell cadmium and lead chalcogenide NCs that have high photoluminescence (PL) QY will be used as light absorbers. The optimal thickness of this shell that balances surface passivation with energy transfer will be experimentally investigated.

2) Self-assembled monolayers of metallic NCs with control of plasmonic properties:
The proposed synthetic platform provides fine control of the metal nanoparticle size, interparticle distance, and

absorber/emitter particle distance. All these factors affect the overlap of the wavefunction between the plasmon and emitter dipole and their resulting electromagnetic interaction. In this geometry, the rate of spontaneous emission may be increased faster than direct modulation with a laser. Can the rate of emission be increased by up to 8 orders of magnitude? Is near-field enhancement or resonance a more important factor?

3) Evaluating the enhancement in photon upconversion by combining (1) and (2):
Thin films from (1) will be spin-coated onto substrates (2) on glass. The upconversion QY will be measured in an integrating sphere, with and without the plasmonic monolayer. The power dependence on the upconversion QY will be recorded. The changes in the radiative and non-radiative rates in the presence and absence of the plasmonic layer will be recorded. All this information will be extremely useful in isolating how the plasmonic nanostructures affect the different steps in this hybrid photon upconversion platform.

Accomplishments: A Bruker AVANCE Neo 400 NMR spectrometer was acquired. This NMR spectrometer provides the breadth and ease of use of a “routine” spectrometer while affording unprecedented sensitivity. It facilitates the characterization of hybrid materials, various combinations of nanocrystals, small molecules or polymers.

The Bruker AVANCE Neo 400 is a user-friendly, state-of-the-art NMR spectrometer capable of performing all modern liquid-state and solid-state NMR experiments. The modular Nanobay design of the spectrometer allows substantial flexibility for future reconfiguration, such as the addition of a cryoprobe. This spectrometer is capable of excellent performance for all modern small molecule and biomolecular NMR experiments, with automated tuning, locking, and shimming abilities insuring reproducible, high quality spectra even for users without significant NMR experience. The TopSpin software chosen for running the spectrometer is very flexible and can easily be configured via a few mouse clicks to allow remote access through secure socket layer connections. The high sensitivity 2H lock channel is ideally suited for research applications in chemistry demanding the highest sensitivity for X nuclei with 1H decoupling as well as excellent 1H or 19F observe sensitivity. The broadband channel covers a wide range of nuclei from 31P to 15N. The outer coil can be used for 1H observation or decoupling and can be tuned to 19F, as well. The probe provides superior 1H line shape and is therefore perfectly suited for indirect detection experiments. It is fitted with a 2H lock channel and an actively shielded z-gradient. This instrument is also capable of precise variable temperature operation at temperatures ranging from –80 ºC to 150 ºC. UCR does not have such a modern NMR.

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Training Opportunities: Here is a list of research groups that have used the instrument since it was installed. It has been the most heavily used instrument in the facility over the time its been here. Researchers that have used this NMR include undergraduates, graduate students and postdoctoral researchers.

Bioengineering
Val Vullev

Botany & Plant Science
Sean Cutler

Chemical and Environmental Engineering
Juchen Guo
Jinyong Liu

Chemistry
Huiwang Ai
Chris Bardeen
Matt Conley
Pingyun Feng
Joey Genereux
Hill Harman
Richard Hooley
Cindy Larive
Catharine Larsen
Vince Lavallo
Dave Martin
Leonard Mueller
Michael Pirrung
Chris Switzer
Ming Lee Tang
Yinsheng Wang
Francisco Zaera

Entomology
Jocelyn Millar

MACReu Grant

Results Dissemination: In conjunction with the Chemistry Club on campus, and as part of the Freshmen Advising Seminar, the Tang group routinely conducts laboratory tours for first year undergraduates or high school students to show the state of the art equipment funded by this equipment grant. These young people are always excited by the drastic color change that occurs during photon upconversion. These laboratory tours occurred in Fall 2016 and Spring 2017.

Honors and Awards: May 2017: Tony Dorado (4th year undergraduate student) won the Best Poster Presentation at the 11th Annual Undergraduate Research Symposium and Danielle Hamilton (3rd year undergraduate student) received the Academic Excellence Award at the 31st Annual Honors Convocation at UCR!

Apr. 2017: Xin Li (5th year graduate student) won an Outstanding Student Poster Award at the 253rd National American Chemical Society Meeting in San Francisco!!!

Feb. 2017: Ming Lee Tang (PI) is one of the 2017 Sloan Research Fellows in Chemistry!

Protocol Activity Status:

Technology Transfer: Nothing to Report

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PARTICIPANTS:

Participant Type: PD/PI
Participant: Ming Lee Tang
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI
Participant: William Hill Harman
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI
Participant: Phillip N Christopher
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Letters
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Date Submitted: 12/12/17 12:00AM Date Published: 10/1/16 7:00AM
Publication Location:
Article Title: Efficient Infrared-to-Visible Upconversion with Subsolar Irradiance
Authors: Melika Mahboub, Zhiyuan Huang, Ming Lee Tang
Keywords: NIR upconversion, solar, core?shell semiconductor quantum dots, acene, triplets, Dexter transfer
Abstract: Third generation photovoltaics are inexpensive modules that promise power conversion efficiencies exceeding the thermodynamic Shockley?Queisser limit, perhaps by using up- or down-converters, intermediate band solar cells, tandem cells, hot carrier devices, or multiexciton generation. Here, we report the efficient upconversion of infrared to visible light at excitation densities below the solar flux. Colloidally synthesized core?shell lead sulfide?cadmium sulfide nanocrystals in combination with tetracene derivatives absorb near-infrared light and emit visible light at 560 nm with an upconversion quantum yield (QY) of 8.4 ± 1.0%, which is a factor of 4 lower than the maximum upconversion QY possible. This is achieved with 808 nm cw excitation at 3.2 mW/cm2, approximately three times lower than the available solar flux. The molecular and nanocrystal engineering here paves the way toward utilizing this hybrid upconversion platform in photovoltaics, photodetectors and photocatalysis.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Angewandte Chemie International Edition
Publication Identifier Type: DOI Publication Identifier: 10.1002/anie.201701929
Volume: 56 Issue: 20 First Page #: 5598
Date Submitted: 12/12/17 12:00AM Date Published: 5/1/17 7:00AM
Publication Location:
Article Title: Complementary Lock-and-Key Ligand Binding of a Triplet Transmitter to a Nanocrystal Photosensitizer
Authors: Xin Li, Alexander Fast, Zhiyuan Huang, Dmitry A. Fishman, Ming Lee Tang
Keywords: bidentate, lock and key, photon upconversion, hybrid
Abstract: Owing to the difficulty in comprehensively characterizing nanocrystal (NC) surfaces, clear guidance for ligand design is lacking. In this work, a series of bidentate bis-(pyridine) anthracene isomers (2,3-PyAn, 3,3-PyAn, 2,2-PyAn) that differ in their binding geometries were designed to find the best complementary fit to the NC surface. The efficiency of triplet energy transfer (TET) from the CdSe NC donor to a diphenylanthracene (DPA) acceptor mediated by these isomers was used as a proxy for the efficacy of orbital overlap and therefore ligand binding. 2,3-PyAn, with an intramolecular N–N distance of 8.2 c, provided the best match to the surface of CdSe NCs. When serving as a transmitter for photon upconversion, 2,3-PyAn yielded the highest upconversion quantum yield (QY) of 12.1:1.3%, followed by 3,3-PyAn and 2,2-PyAn. The TET quantum efficiencies determined by ultrafast transient absorption measurements showed the same trend.
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Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Communications
Publication Identifier Type: DOI Publication Identifier: 10.1039/C6CC08229G
Volume: 53 Issue: 7 First Page #: 1241
Date Submitted: 12/12/17 12:00AM Date Published:
Publication Location:
Article Title: On the efficacy of anthracene isomers for triplet transmission from CdSe nanocrystals
Authors: Pan Xia, Zhiyuan Huang, Xin Li, Juan J. Romero, Valentine I. Vullev, George Shu Heng Pau, Ming Lee
Keywords: isomers, anthracene, CdSe, photon upconversion
Abstract: The effect of isomeric substitutions on the transmitter for triplet energy transfer (TET) between nanocrystal (NC) donor and molecular acceptor is investigated. Each isomeric acceptor is expected to bind in a unique orientation with respect to the NC donor.We see that this orbital overlap drastically affects the transmission of triplets.Here, two functional groups, the carboxylic acid and dithiocarbamate, were varied between the 1-, 2- and 9-positions of the anthracene ring to give three ACA and three ADTC isomers. These six anthracene isomers served as transmitters for triplets between CdSe NC sensitizers and 9,10-diphenylanthracene annihilators for photon upconversion. The photon upconversion quantum yield (QY) is the highest for 9-ACA (12%), lowest for 9-ADTC (0.1%), around 3% for both 1-ACA and 1-ADTC, and about 1% for the 2-isomers. These trends in QYs are reflected in the rates of TET given by ultrafast transient absorption spectroscopy
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

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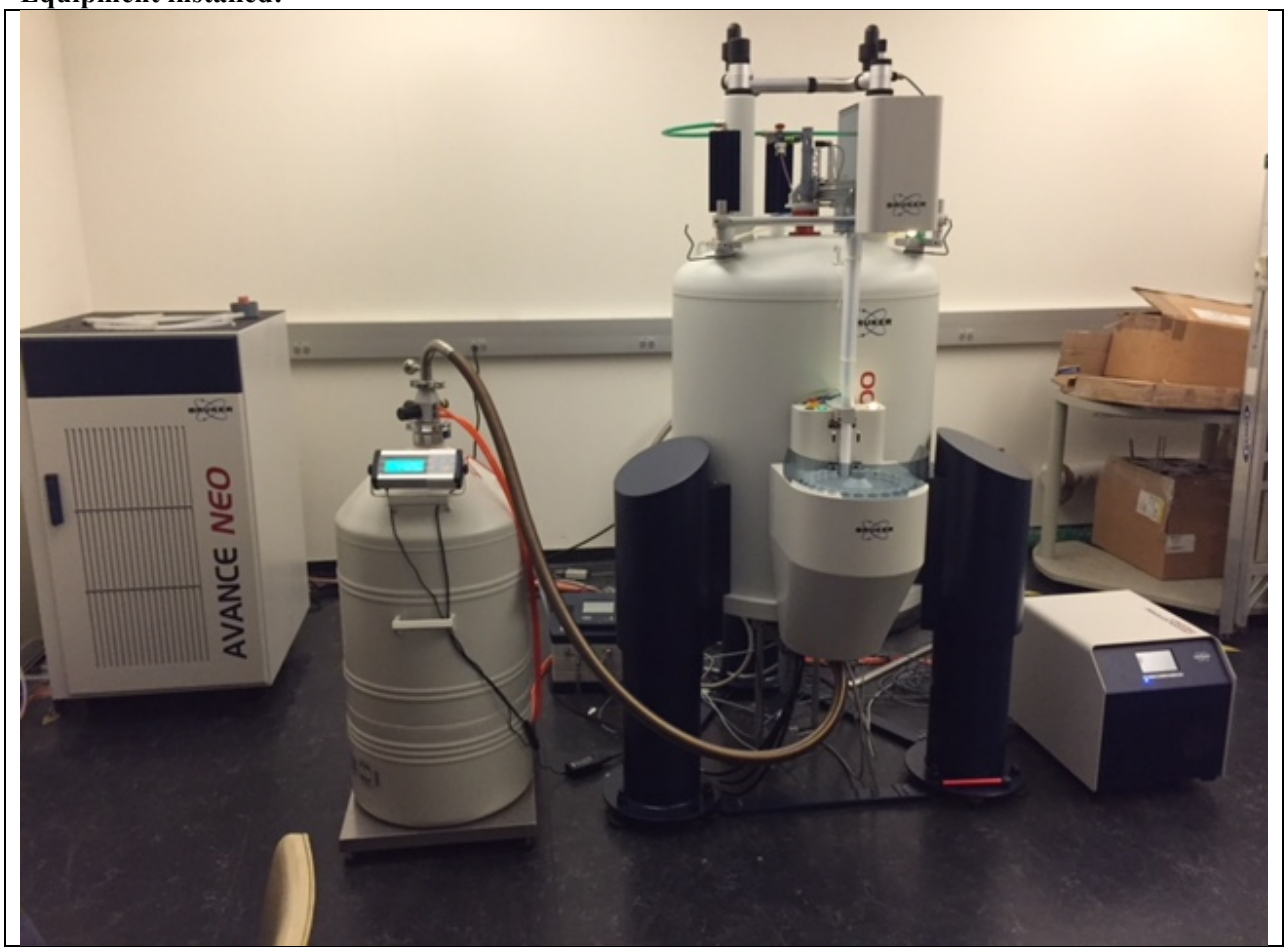
as of 01-Mar-2018

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Science
Publication Identifier Type: DOI Publication Identifier: 10.1039/C7SC01610G
Volume: 8 Issue: 8 First Page #: 5488
Date Submitted: 12/12/17 12:00AM Date Published:
Publication Location:
Article Title: CdS/ZnS core–shell nanocrystal photosensitizers for visible to UV upconversion
Authors: Victor Gray, Pan Xia, Zhiyuan Huang, Emily Moses, Alexander Fast, Dmitry A. Fishman, Valentine I. Vul
Keywords: visible to ultra-violet upconversion
Abstract: Herein we report the first example of nanocrystal (NC) sensitized triplet–triplet annihilation based photon upconversion from the visible to ultraviolet (vis-to-UV). Many photocatalyzed reactions, such as water splitting, require UV photons in order to function efficiently. Upconversion is one possible means of extending the usable range of photons into the visible. Vis-to-UV upconversion is achieved with CdS/ZnS core–shell NCs as the sensitizer and 2,5-diphenyloxazole (PPO) as annihilator and emitter. The ZnS shell was crucial in order to achieve any appreciable upconversion. From time resolved photoluminescence and transient absorption measurements we conclude that the ZnS shell affects the NC and triplet energy transfer (TET) from NC to PPO in two distinct ways. Upon ZnS growth the surface traps are passivated thus increasing the TET. The shell, however, also acts as a tunneling barrier for TET, reducing the efficiency.

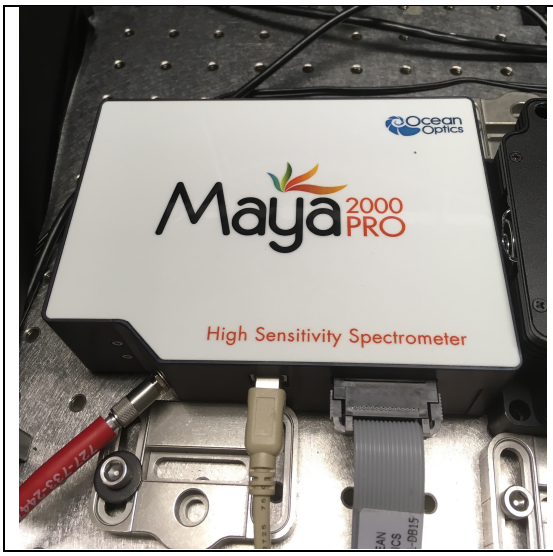
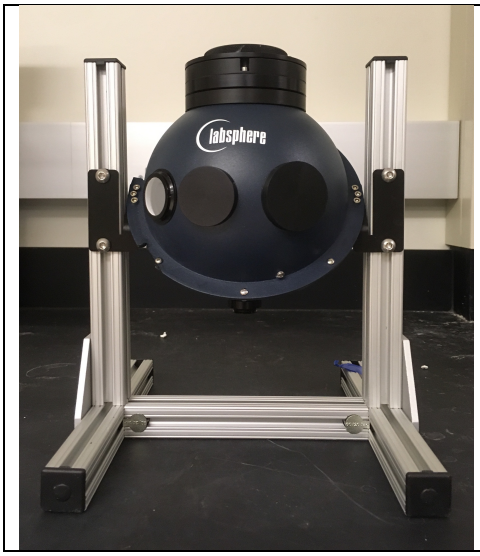
Acknowledged Federal Support: **Y**

Proposal Number: 68838MSREP; Agreement Number: W911NF1610523
Proposal Title: Plasmonic nanocrystals for enhanced hybrid photon upconversion.

Equipment installed:



The Bruker AVANCE Neo 400 is a user-friendly, state-of-the-art NMR spectrometer capable of performing all modern liquid-state and solid-state NMR experiments. The modular Nanobay design of the spectrometer allows substantial flexibility for future reconfiguration, such as the addition of a cryoprobe. This spectrometer is capable of excellent performance for all modern small molecule and biomolecular NMR experiments, with automated tuning, locking, and shimming abilities insuring reproducible, high quality spectra even for users without significant NMR experience. The TopSpin software chosen for running the spectrometer is very flexible and can easily be configured via a few mouse clicks to allow remote access through secure socket layer connections. The high sensitivity ^{2}H lock channel is ideally suited for research applications in chemistry demanding the highest sensitivity for X nuclei with ^{1}H decoupling as well as excellent ^{1}H or ^{19}F observe sensitivity. The broadband channel covers a wide range of nuclei from ^{31}P to ^{15}N. The outer coil can be used for ^{1}H observation or decoupling and can be tuned to ^{19}F, as well. The probe provides superior ^{1}H line shape and is therefore perfectly suited for indirect detection experiments. It is fitted with a ^{2}H lock channel and an actively shielded z-gradient. This instrument is also capable of precise variable temperature operation at temperatures ranging from –80 ºC to 150 ºC.

	The Maya Pro is a spectrometer that can be configured to measure either absorption or fluorescence from the UV to the NIR (400-1100 nm). Note the Maya Pro, Labsphere Integrating Sphere and Coherent laser are used together to measure the photon upconversion or photoluminescence quantum yields of thin films created in this project.
	This Labsphere Integrating Sphere is for accurate measurements of the absolute quantum yields for the photon upconverting thin films
	This Coherent 785 nm solid state OBIS laser has a Gaussian profile. Its excitation density can be accurately and reproducibly changed.

Proposal Number: 68838MSREP; Agreement Number: W911NF1610523
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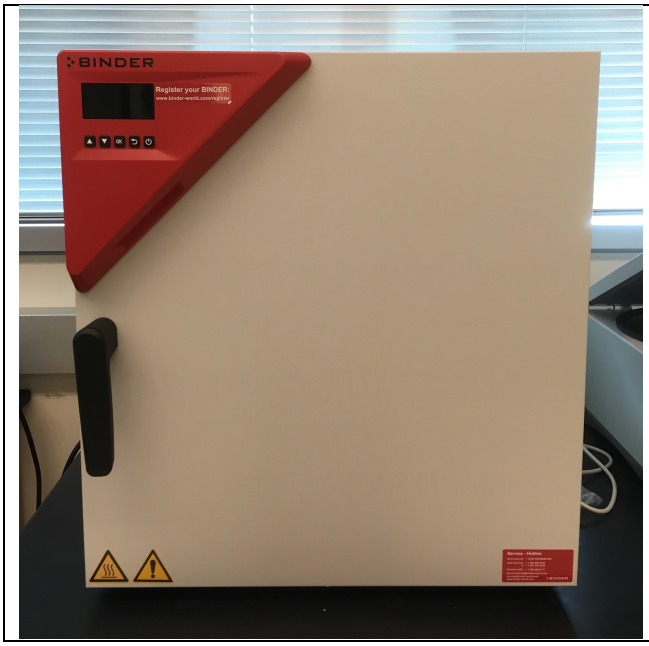	This Binder oven is used for drying substrates and the thin films created in this project.
	This WaveDriver 10 Potentiostat/Galvanostat from Pine Resesarch includes AfterMath Software (WaveDriver 10, single instrument license) and a Cell Cable (for WaveDriver 10 Potentiostat/Galvanostat). Accessories like electrodes and electrochemical cells were also purchased. This instrument enables measurement of the energy levels in semiconductor nanocrystals and small molecules, i.e. the conduction/ valence bands for the former, and the highest occupied and lowest unoccupied molecular orbitals (HOMO/ LUMO) for the latter.